



Z-scheme system of WO₃@MoS₂/CdS for photocatalytic evolution H₂: MoS₂ as the charge transfer mode switcher, electron-hole mediator and cocatalyst

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ABSTRACT

A novel ternary Z-scheme system of WO₃@MoS₂/CdS is successfully constructed using a three-step wet-chemical route, where MoS₂ locates between the rod-shaped WO₃ and CdS nanoparticles and simultaneously plays multiple roles of the charge transfer mode switcher, electron-hole mediator and cocatalyst. As a charge transfer mode switcher, MoS₂ can transform the conventional type-II charge transfer mode to Z-scheme. In such a Z-scheme system, as an electron-hole mediator, MoS₂ is applied to quench the energy of the electrons from WO₃ and the holes from CdS in shorten length, and thus the more left electrons from CdS can transfer to MoS₂, which can be further applied to photocatalytic evolution H₂ owing to the cocatalyst role of MoS₂. Benefitting from the multifunctional roles of MoS₂, such a Z-scheme system of WO₃@MoS₂/CdS shows an enhanced photocatalytic performance.

1. Introduction

Semiconductor driven photocatalysis has long been emerged as an attractive protocol to environmental pollution and energy crisis [1–5]. To date, many efforts have been made to enhance the photocatalytic efficiency, and among them, construction of type-II heterostructure can be seen as a potential strategy due to its extended light absorption range and decreased recombination of charge carriers compared with individuals [6,7]. Usually, this kind of heterostructure contains two charge carrier transfer modes of conventional type-II and Z-scheme [8]. As is known, the efficient charge separation of conventional type-II is at the cost of its redox ability [9–11]. Therefore, in order to achieve the excellent performance and wide application prospect, compared with conventional type-II, Z-scheme mode, which simultaneously possesses the high charge separation efficiency and strong redox property, is more potential and suitable [12–17]. Thus, many researches are focused on directly conducting a Z-scheme system [18,19]. Nevertheless, how to switch the charge transfer mode from conventional type-II to favor Z-scheme is more challenging and extensive.

Besides, in a Z-scheme system, enhancing the transfer rate of electron on the interface of PS I (photosystem I, where the photogenerated holes with a lower oxidation ability) and PS II (photosystem II, where the photogenerated electrons with a lower reduction ability) is very

urgent. Up to now, many shuttle redox mediators have been applied to accelerate the electrons transfer. Unfortunately, there are also some limitations. For reversible redox mediators, backward reactions are easily happened, and its application is only constrained in liquid phase reactions [16,20]. For solid electron mediator, the noble metals (Au, Ag and so on) and graphene are usually explored. In addition to the high cost, all of them only can transfer electrons rather than both of electrons and holes [21–25]. In this case, only the electrons from PS II can transfer to PS I, leading to too long transmission distances, which provides opportunity for charges recombination on the interface. Therefore, if introducing an electron-hole mediator into Z-scheme system, which not only transfer electrons, but the holes, the electrons from PS II will be recombined with the holes from PS I in this mediator, which just like “iceberg” for quenching the energy of these charge carriers. Thus, the transmission distances can be greatly shortened, which can contribute to promote the favor separation and transfer of charge carriers, leading to the enhanced performance.

Thus, in a Z-scheme system contained electron-hole mediator, more electrons from PS I and holes from PS II are left to participate in photocatalytic reaction. Nevertheless, if these charge carriers can't be consumed in time, the recombination will happen again on the surface. Therefore, in order to further accelerate surface separation of carriers and improve the efficiency of photocatalyst systems, cocatalyst loading,

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as an effective way, has been widely studied [26,27]. The main roles of such cocatalyst are to collect photogenerated charge carriers and host active sites for surface chemical reactions by the carriers [28–31]. However, extra introducing cocatalyst into Z-scheme system may increase the cost of materials. Therefore, if a potential candidate can simultaneously play multiple roles such as switching the charge transfer mode, electron-hole mediator and cocatalyst, the performance of Z-scheme system will be improved significantly.

Herein, a novel model structure $\text{WO}_3/\text{MoS}_2/\text{CdS}$, where the MoS_2 locates at WO_3/CdS interface, is successfully constructed using a three-step wet-chemical route. As a charge transfer mode switcher, MoS_2 can transform the conventional type-II charge transfer mode to Z-scheme. As an electron-hole mediator, MoS_2 can both transfer electrons and holes, where MoS_2 just like an “iceberg” to quench the energy of the electrons from WO_3 and the holes from CdS in shorten length. As a cocatalyst, the CB of MoS_2 can provide active sites for photocatalytic evolution H_2 driven by the electrons from CdS . Since MoS_2 simultaneously acts as the mentioned functions, the $\text{WO}_3/\text{MoS}_2/\text{CdS}$ can be shown an improved photocatalytic performance compared with WO_3/CdS or MoS_2/CdS .

2. Experimental procedures

2.1. Materials

Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), sodium chloride (NaCl), concentrated hydrochloric acid (HCl), absolute ethanol, glucose solution, sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), thiourea ($\text{CH}_4\text{N}_2\text{S}$), $\text{Cd}(\text{CH}_3\text{COO})_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). The above chemical reagents were of analytical grade and without further purification. Deionized (DI) water was used throughout this work.

2.2. Synthesis of photocatalysts

2.2.1. Preparation of WO_3

The WO_3 was prepared according to previous literatures [32]. In a typical synthesis, 1 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 0.5 g of NaCl were dissolved in 20 mL of water. The pH of the solution was adjusted to 2 by 4 M HCl . The above solution was stirred for 60 min and then transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 180°C for 24 h. After cooled down to room temperature, the sample was centrifugalized with distilled water and absolute ethanol several times and dried in a 60°C oven.

2.2.2. Preparation of WO_3/MoS_2

WO_3/MoS_2 was prepared through the following process [33,34]. 0.1 g WO_3 was added to 30 mL of glucose solution (0.5 M) and ultrasound 20 min. Then 0.5 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 1 g of $\text{CH}_4\text{N}_2\text{S}$ were added and stirring for 30 min. The mixed solution was then transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 200°C for 12 h. Finally, the as-obtained sample was centrifugalized with distilled water and absolute ethanol several times.

2.2.3. Preparation of $\text{WO}_3/\text{MoS}_2/\text{CdS}$

$\text{WO}_3/\text{MoS}_2/\text{CdS}$ was fabricated by chemical bath deposition according to literature [15]. Typically, 50 mg of WO_3/MoS_2 sample was added in 60 mL de-ionized water containing 1 g $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Subsequently, the above suspension was stirred for 30 min in dark. 0.6 g $\text{CH}_4\text{N}_2\text{S}$ was then added to the suspension. After the chemical bath deposition at 80°C for 20 min, the precipitate was collected by centrifugation and washed with de-ionized water several times.

2.2.4. Preparation of WO_3/CdS

WO_3/CdS was synthesized by the method similar to $\text{WO}_3/\text{MoS}_2/\text{CdS}$ but adding WO_3 instead of WO_3/MoS_2 .

2.2.5. Preparation of MoS_2/CdS

MoS_2/CdS was synthesized by the method similar to $\text{WO}_3/\text{MoS}_2/\text{CdS}$ but adding MoS_2 instead of WO_3/MoS_2 .

For comparison, the pure MoS_2 and CdS were synthesized under the same experimental conditions, respectively.

2.2.6. Preparation of CdS

CdS was synthesized by the method similar to WO_3/CdS but without adding WO_3 .

2.2.7. Preparation of MoS_2

MoS_2 was synthesized by the method similar to WO_3/MoS_2 but without adding WO_3 .

2.3. Characterization

The crystal structure of as-prepared samples were carried out by a Bruker D8 ADVANCE X-ray diffraction with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$), which operated at 40 kV and 40 mA. The morphologies were obtained with a HITACHI SU8000 field-emission scanning electron microscope (SEM) and a transmission electron microscope (TEM) and high-resolution transmission electron micrographs (HRTEM, FEI Tecnai G20) with an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) was characterized by a Thermo Scientific ESCA Lab 250 system, with a monochromatic Al K α as the X-ray source, hemispherical analyzer. The UV–Vis diffuse reflectance spectra (DRS) of samples were measured by a Carry 5000 UV–vis spectrophotometer, where BaSO_4 was served as the background. Photoluminescence spectrum was obtained using a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer with a 425 nm excitation wavelength.

2.4. Photoelectrochemical measurements

The photoelectrochemical properties of the samples were measured in a conventional three-electrode electrochemical workstation (CHI 660E, CH Instruments, Inc., Shanghai) with Ag/AgCl electrode as the reference electrode and Pt wire as the counter electrode. 0.2 M of aqueous Na_2SO_4 solution was used as the supporting electrolyte. The sample electrode was prepared according to the following process: 50 mg sample was suspended in 0.5 mL of $\text{C}_2\text{H}_5\text{OH}$, which was used for spreading the sample onto the Fluorinedoped Tin Oxide (FTO) glass of $0.5 \times 0.5 \text{ cm}$. The sample electrode was irradiated by a 300 W Xe arc lamp. Electrochemical impedance spectroscopy (EIS) under AC polarization (10 mV) was measured on another Potentiostat (ZAHNER).

2.5. Photocatalytic activity measurements

The photocatalytic activities of samples were evaluated by photocatalytic H_2 evolution reaction. Typically, 30 mg photocatalyst was suspended in 100 mL mixed aqueous solution containing 10 vol.% of lactic acid, and then performed in a relatively vacuum system allocated an external glass reaction cell by the Labsolar-6A photocatalytic water decomposition hydrogen production system (Perfect light Technology Co. Ltd.). The suspension was degassed for 30 min to remove all air in solution and headspace. Then the vessel was vertically irradiated by a 300 W Xe lamp. The temperature of reaction solution was maintained at 5°C . The amount of generated H_2 was analyzed by a Techcomp GC7900 gas chromatograph with a thermal conductivity detector (TCD, molecular sieve 5A, argon carrier gas 99.999%).

3. Results and discussion

3.1. Structural properties of photocatalysts

The crystal structure and phase purity of as-synthesized materials are characterized by X-ray diffraction (XRD) analysis. As shown in

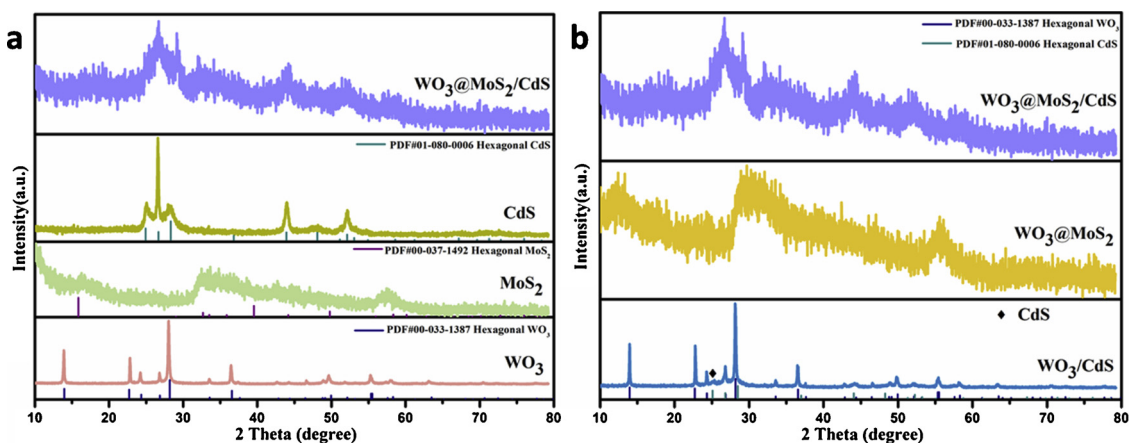


Fig. 1. XRD patterns of all samples.

Fig. 1a, the sharp peak patterns of WO_3 , MoS_2 and CdS are well matched with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card No. 00-033-1387, No. 00-037-1492 and No. 01-080-0006, which is assigned to hexagonal WO_3 , hexagonal MoS_2 and hexagonal CdS , respectively. As shown in Fig. 1b, it can be seen that the diffraction peak of CdS are more clearly shown at about 25.02° in the XRD pattern of WO_3/CdS . And combining with the SEM images of WO_3 and WO_3/CdS shown in Fig. S1, it can be clearly seen that CdS nanoparticles are deposited onto the surface of WO_3 , indicating that CdS is successfully deposited onto the WO_3 . Besides, since only the diffraction peaks of CdS and MoS_2 appear on the XRD pattern of the $\text{WO}_3@/\text{MoS}_2/\text{CdS}$, and considering the preparation sequence of samples, it is considered that MoS_2 may wrap on the surface of WO_3 , and CdS may be deposited on MoS_2 [7,34]. Thus, MoS_2 may locate between WO_3 and CdS . This hypothetical model also needs to be further confirmed by subsequent SEM and TEM characterizations.

SEM and TEM characterizations are further applied to obtain morphological and positional information of as-prepared samples. As displayed in Fig. 2a, pure WO_3 shows rod-like structure with a diameter of 150 nm and a length of 1–2 μm and relatively smooth surface. In Fig. 2b, MoS_2 nanosheets are grown on the surface of the WO_3 rods uniformly, and WO_3 is encapsulated by MoS_2 . As shown in Fig. 2c, the

smooth MoS_2 nanosheets surfaces are roughened with the CdS uniformly grown on the surface of MoS_2 . TEM investigation is applied to further confirm the crystal structures and morphologies of $\text{WO}_3@/\text{MoS}_2/\text{CdS}$. As shown in Fig. 2e and f, the lattice fringe of CdS displays spacing of 0.355 nm, which matches well with the (100) plane of the hexagonal CdS . Fig. 2f shows a relatively blurry characteristic spacing of 0.316 nm, corresponding to the (200) lattice plane of hexagonal WO_3 . The relatively blurry lattice fringe of WO_3 may be attributed to the encapsulation by MoS_2 . Besides, Fig. 2d shows the WO_3 and CdS are isolated by MoS_2 , which is consistent with the mentioned results of XRD and SEM.

3.2. Photocatalytic activity and stability

To date, we have successfully proved the composition and structure of $\text{WO}_3@/\text{MoS}_2/\text{CdS}$. Then the photocatalytic H_2 evolution performances of aforementioned composites are evaluated shown in Fig. 3. The activity of WO_3 is hardly detectable owing to its too positive CB potential. And $\text{WO}_3@/\text{MoS}_2$ is almost inactive due to rapid recombination of photoinduced charge carriers of MoS_2 . Besides, pure CdS shows very low activity ($0.02 \text{ mmol h}^{-1} \text{ g}^{-1}$) because of rapid recombination of charge carriers. WO_3/CdS shows relatively low activity (0.21 mmol

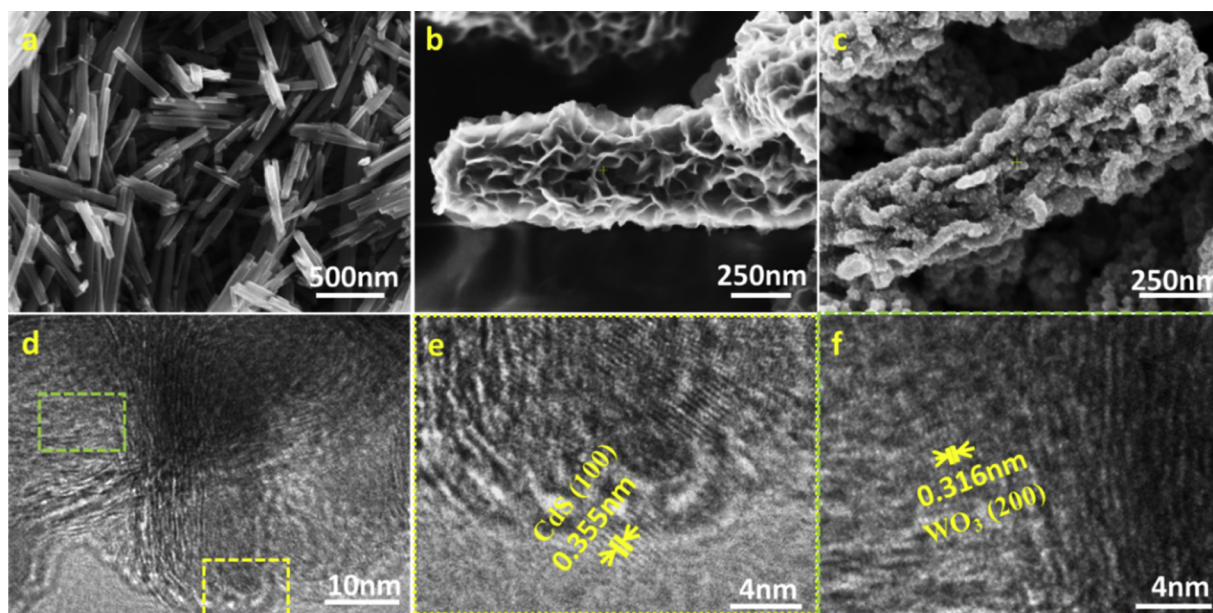


Fig. 2. Typical SEM images of WO_3 (a), $\text{WO}_3@/\text{MoS}_2$ (b), $\text{WO}_3@/\text{MoS}_2/\text{CdS}$ (c), TEM image of $\text{WO}_3@/\text{MoS}_2/\text{CdS}$ (d) and HRTEM images (e) and (f) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

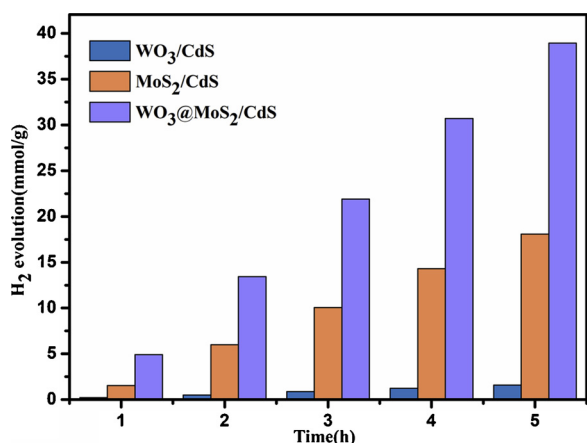


Fig. 3. Photocatalytic H₂ evolution rates of composites.

$\text{h}^{-1} \text{g}^{-1}$), which might be attributed to its charge transfer of conventional type-II. The corresponding evidences can be given by XPS data. The activity of MoS₂/CdS is relatively high ($3.6 \text{ mmol h}^{-1} \text{g}^{-1}$) owing to the cocatalyst role of MoS₂, which can enhance the charge separation and provide active site for photocatalytic evolution H₂. Obviously, WO₃@MoS₂/CdS composite presents the maximum H₂ evolution ($8.2 \text{ mmol h}^{-1} \text{g}^{-1}$) than WO₃/CdS or MoS₂/CdS. The enhanced performance is usually attributed to the decreasing recombination of photogenerated electron-hole pairs and increasing numbers of favor charge carriers, which may be caused by MoS₂. Therefore, the following part is to demonstrate the multifunctional roles of MoS₂, which not only switches the charge transfer mode from type-II to Z-scheme, but acts as electron-hole mediator to shorten interface transmission distance and cocatalyst for providing active sites. Besides, as shown in Fig. S2, the novel Z-scheme system of WO₃@MoS₂/CdS present a satisfying stable performance for hydrogen production during a 12 h cycling test without refreshing the catalysts and sacrificial agents.

In order to demonstrate the roles of MoS₂ in enhancing performance of WO₃@MoS₂/CdS, XPS investigation can be seen as powerful evidence. After WO₃@MoS₂/CdS and WO₃/CdS are undergone the same photocatalysis process, the two samples are referred to WO₃@MoS₂/CdS-used and WO₃/CdS-used, respectively. As displayed in Fig. 4, the W 4f XPS spectra of pure WO₃ shows two dominant peaks, which are corresponded to W⁶⁺ ions. While there are four peaks in WO₃/CdS-used, the peaks at 37.7 and 35.6 eV are corresponded to W⁶⁺ ions, and the dominant peaks at 36.3 and 34.1 eV are corresponded to W⁵⁺ ions. This result of multiple valence states of W demonstrates the electrons

from CdS do transfer to WO₃, and the change transfer manner of WO₃/CdS is traditional type-II [8,32]. In the W 4f XPS spectra of WO₃@MoS₂/CdS-used, there are two dominant peaks, which are corresponded to W⁶⁺ ions, indicating that there may be no electrons transfer to WO₃, and the change transfer mode of WO₃@MoS₂/CdS may follow Z-scheme. These results also can further demonstrate that MoS₂ is vertically located on the WO₃ without horizontal coating. In this case, WO₃ can be excited by light to produce photogenerated charge carriers. Besides, owing to electron migration can cause a shift in the binding energy of a specific element, the charge transfer also can be further proved by XPS patterns. According to Fig. 4, a respective negative shift of W 4f state in the binding energy of WO₃/CdS-used compared with WO₃ can be clearly observed, indicating the photogenerated electrons are moved from CdS to WO₃, which is accordance with the result of multiple valence states of W. While in WO₃@MoS₂/CdS-used, the way of electron transfer is inverted: W 4f binding energy is shifted in positive direction compared with WO₃, which reveals the electrons from WO₃ are transferred to MoS₂. According to the aforementioned analyzes, it can be concluded that MoS₂ can be as a charge transfer mode switcher for transforming the conventional type-II to Z-scheme.

In order to further investigate the effect of MoS₂ on the interfacial charge transfer properties, electrochemical impedance spectroscopy (EIS) and transient photocurrent responses of as-synthesized materials are implemented. As shown in Fig. 5a and b, it is found that WO₃@MoS₂/CdS has a smallest radius of the semi-cycle arc in the Nyquist plot compared with that of other samples, which signifies that a more efficient interfacial charge transfer of WO₃@MoS₂/CdS on the electrode/electrolyte interface. As shown in Fig. 5c and d, it is worth noting that WO₃@MoS₂/CdS shows significantly enhanced photocurrent densities, which means that more effective charge separation and transmission is realized. These results further confirm that introducing MoS₂ into WO₃/CdS can facilitate the surficial charge transfer and lead to an effective separation of photogenerated charge carriers, which induced a prominent increment of performance in the photocatalytic hydrogen process.

To further investigate the transfer and separation efficiency of the charge carriers, the photoluminescence (PL) spectra is employed and shown in Fig. S3. CdS displays a strong emission peak located at 580 nm, and WO₃/CdS and MoS₂/CdS both exhibit a relatively weak intensity. Moreover, WO₃@MoS₂/CdS shows a weaker PL intensity even than MoS₂/CdS, demonstrating that the novel Z-scheme system can further inhibit the photogenerated carrier recombination of CdS. As a consequence, these results are in accordance with the XPS, EIS and transient photocurrent responses data analysis above, which confirm the multifunctional roles of MoS₂ in enhancing performance of WO₃@MoS₂/CdS.

Besides, the photocatalytic performance is also related to the photo-response characteristics of the photocatalyst. Thus, the optical absorption region needs to be confirmed and discussed in detail below. The optical properties of the as-prepared samples are investigated via UV-vis diffuse reflectance spectroscopy (DRS) shown in Fig. 6. Bare WO₃ shows a narrow absorption, and CdS exhibits a relatively wide absorption. Obviously, MoS₂ has a wide absorption in the visible-light region. According to Fig. 6b, WO₃/CdS shows a weaker absorption compared with the other three samples. Notably, WO₃@MoS₂/CdS exhibits a wider absorption than MoS₂/CdS, which means more photogenerated charge carriers can participate in photocatalytic reaction. Besides, the photocatalytic activities of WO₃@MoS₂/CdS and MoS₂/CdS are compared under light irradiation of single wavelength at 475 nm to sure WO₃ can't be excited. In this case, this activity of both can reflect the effect of existential state of MoS₂ on photocatalytic performance. As shown in Fig. S4, MoS₂/CdS shows higher performance compared with WO₃@MoS₂/CdS, which mainly due to the less mass of MoS₂/CdS in WO₃@MoS₂/CdS than that in MoS₂/CdS. Therefore, this result shows the importance of WO₃, and further confirms the electron-hole mediator role of MoS₂ is one of the main reasons to enhance photocatalytic performance.

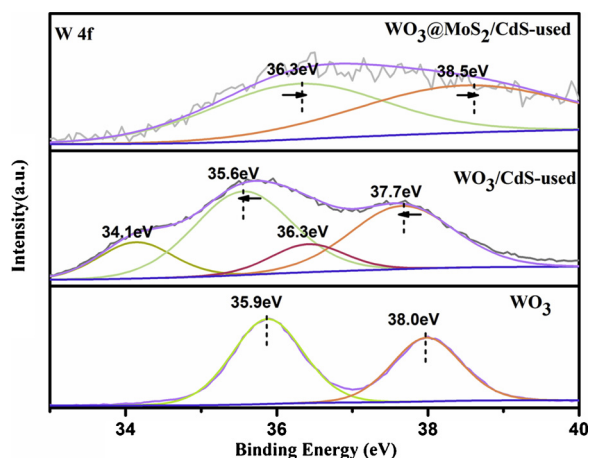


Fig. 4. (a) W 4f XPS spectra of WO₃, WO₃/CdS-used and WO₃@MoS₂/CdS-used.

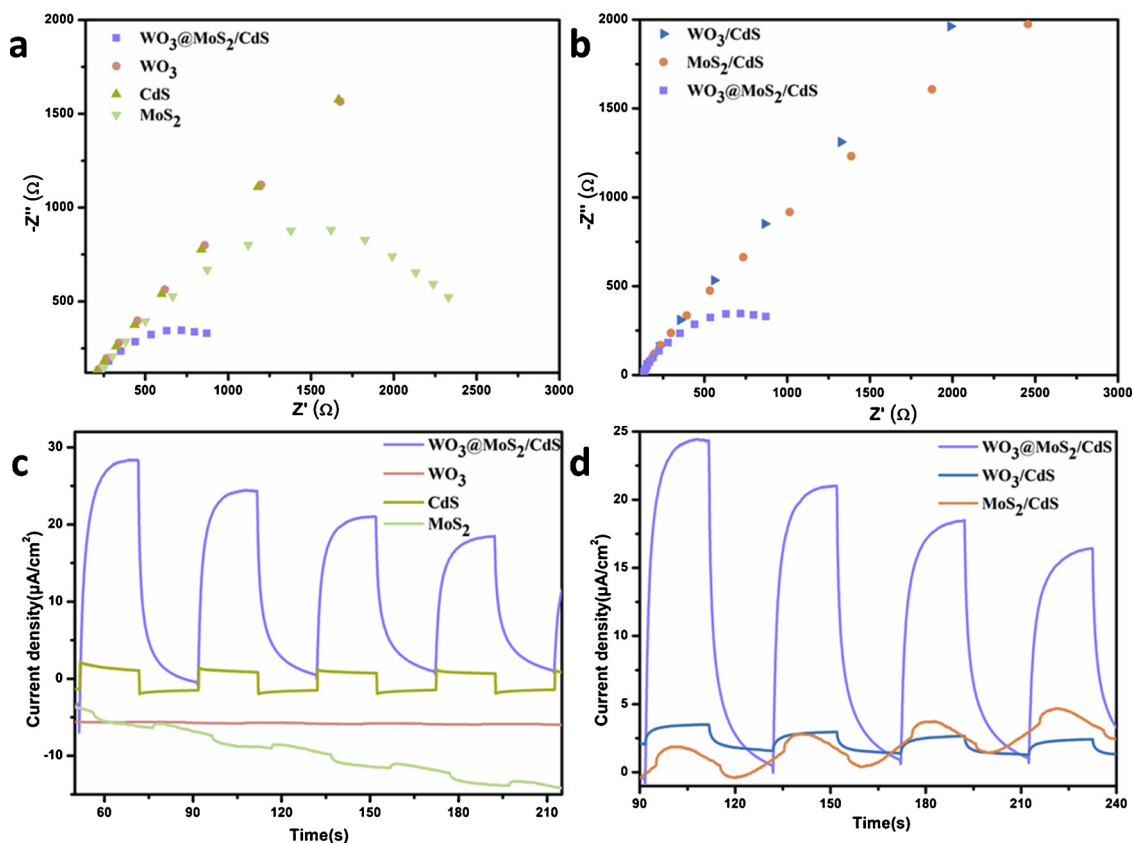


Fig. 5. photo-electrochemical impedance spectra (a) and transient photocurrent responses (b) of all samples.

3.3. Photocatalytic mechanism

Before proposing the mechanism for the photocatalytic H_2 production, the energy level structure of WO_3 , MoS_2 and CdS should be ascertained. According to Fig. S5, the E_g of WO_3 and CdS are 2.86 and 2.23 eV, respectively. As Fig. S6 shown, the VB of WO_3 and CdS are 3.18 and 1.86 V respectively, which are measured by XPS data. According to $E_{CB} = E_{VB} - E_g$, the CB of WO_3 and CdS are 0.32 and -0.37 eV, respectively. Owing to strong light absorption of MoS_2 , it's difficult to measure the E_g of MoS_2 . Therefore, by referencing to corresponding literatures [34], the CB and VB of MoS_2 are -0.14 and 1.78 eV, respectively. Based on the above test results, the CB and VB positions of the three semiconductors are drawn in Fig. 7.

On the basis of the mentioned results, the mechanism for the photocatalytic H_2 production by $WO_3@MoS_2/CdS$ can be clearly proposed.

As depicted in Fig. 7, both WO_3 and CdS can simultaneously be excited and generate electron-hole pairs. The photo-induced electrons on the CB of WO_3 and holes from VB of CdS both can be transferred to MoS_2 ("iceberg") and then recombined. In this case, the transmission distances can be shortened significantly, leading to promote the favor separation and transfer of charge carriers, and the whole transfer mode of charge carriers follows Z-scheme mechanism. In this case, the more electrons on the CB of CdS can be moved to MoS_2 , which provides active sites for the photocatalytic process, leading to high performance of H_2 production.

4. Conclusions

In summary, a novel model structure $WO_3@MoS_2/CdS$, where the MoS_2 locates at the interface of WO_3/CdS , is successfully constructed

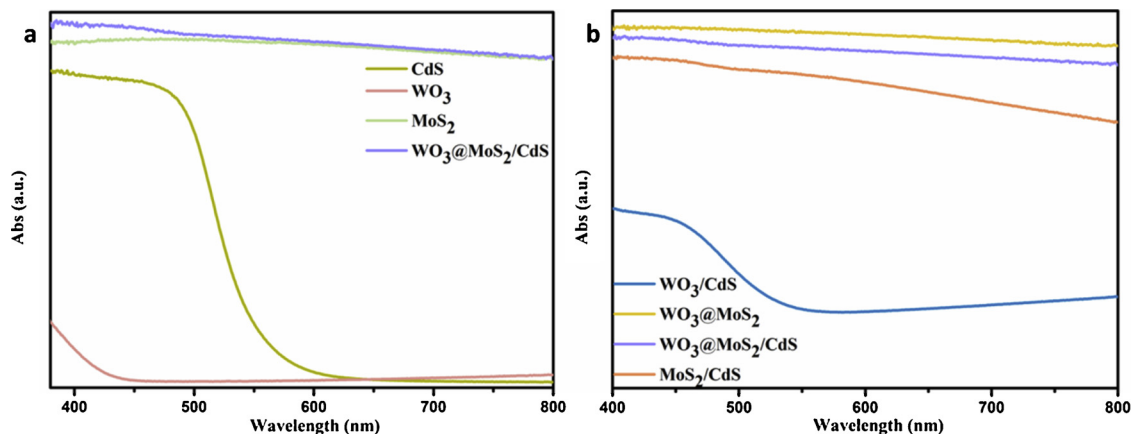


Fig. 6. (a) UV-vis diffuse reflectance spectrum of samples.

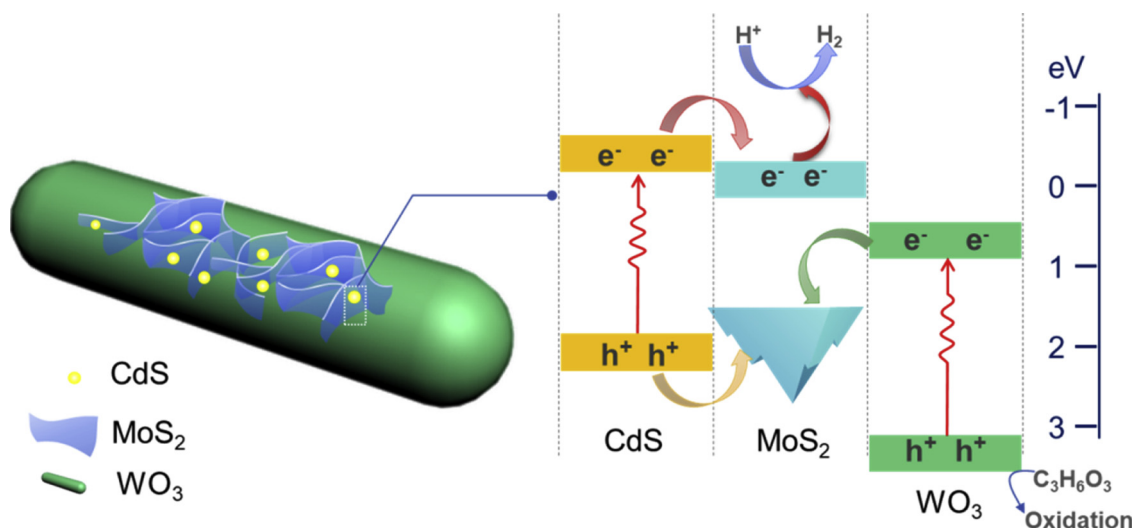


Fig. 7. Proposed mechanisms of $\text{WO}_3@ \text{MoS}_2/\text{CdS}$ for photocatalytic H_2 evolution.

using a three-step wet-chemical route. There are three function roles of MoS_2 in $\text{WO}_3@ \text{MoS}_2/\text{CdS}$: charge carriers transfer switcher, electron-hole mediator and co-catalyst. Such established $\text{WO}_3@ \text{MoS}_2/\text{CdS}$ offers a new strategy for the development of effective Z-scheme systems, which further improve the photocatalytic performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.118073>.

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